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PREPARATION AND PROPERTIES OF DERIVATIVES OF DITHIOLYLIDENE-(4'-PHENYLDIAZONIUM)ACETONITRILE

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The fluoroborates of (4,5-dimethyl-1,3-dithiolylidene)-(4'-phenyldiazonium)acetonitrile and (4,5-ethylenedithio-1,3-dithiolylidene)-(4'-phenyldiazonium)acetonitrile have been prepared; these compounds are photosensitive in the visible region of the spectrum. The quantum yield in the photolysis of the fluoroborates in acetonitrile solution amounts to 0.1 mole/einstein.

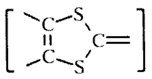
A scan of new phenyldiazonium salts of heterocyclic derivatives which are photosensitive in the visible region opens up the possibility of developing colored diazophotomaterials [1]. The structures of such diazonium derivatives are built up as follows:

$$D-M-ArN_2^+,$$

where D is the fragment with electron-donor properties; M is the bridging structure which achieves partial conjugation of the donor part of the molecule (D) with the electron acceptor ArN_2^+.

A long-wave shift of the absorption band can be realized by increasing both the electron-donor properties of the fragment D and of the bridging structure M.

We have selected dithiolylidene



as the strong electron-donor fragment. The fluoroborates of (4,5-dimethyl-1,3-dithiolylidene)-(4'-phenyldiazonium)acetonitrile and (4,5-ethylenedithio-1,3-dithiolylidene)-(4'-phenyldiazonium)acetonitrile were prepared according to the following scheme:

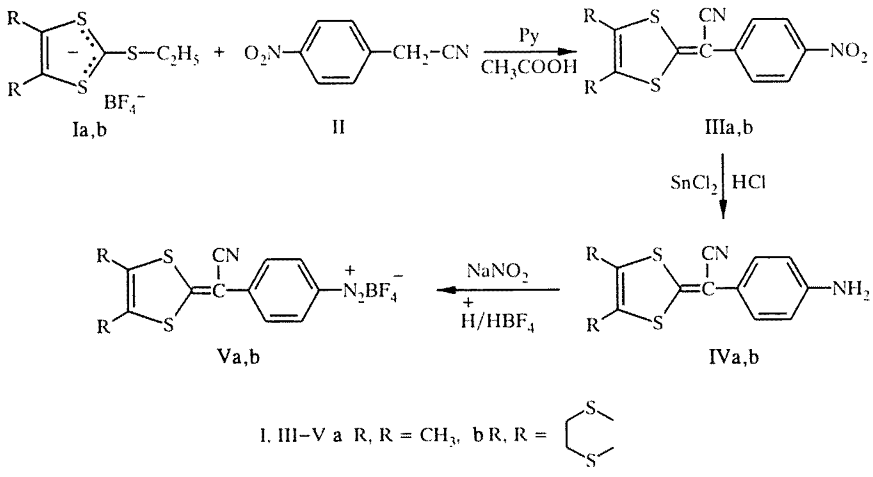


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TABLE 1. Characteristics of Intermediates and Diazonium Salts

Compound	Empirical formula	mp, °C	Electronic spectrum in ethanol, λ_{max}nm (lg ε)	IR spectrum, ν cm^{-1}	Yield %
IIIa	$C_{13}H_{10}N_2O_2S_2$	236	231 (4,08), 269 (4,02), 324 (3,68), 430 (4,39)	1508, 1545, 1580, 2198	79
IIIb	$C_{13}H_8N_2O_2S_4$	201	267 (4,15), 447 (4,06)	1507, 1528 n, 1590, 2198	80
IVa	$C_{13}H_{12}N_2S_2$	166	265 (4,13), 379 (4,28)	1545, 1620 n, 1634, 2180, 3352, 3436	85
IVb	$C_{13}H_{10}N_2S_4$	156	244 (4,25), 312 (3,98), 392 (4,23)	1540, 1625, 1640, 2930, 3208, 3316	79
Va	$C_{13}H_{10}N_3S_2BF_4$	—	525 (4,53)*	2202, 2245*^{2}	56
Vb	$C_{13}H_8N_3S_4BF_4$	—	535 (4,51)*	2200, 2241*^{2}	49

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*Electronic spectrum in acetonitrile in range 380-700 nm.

**IR spectrum in range 2000-2500 cm^{-1} (n = inflection).

Condensation of the fluoroborates of the 2-ethylmercapto-1,3-dithiolium derivatives (Ia, Ib) with 4-nitrobenzyl cyanide (II) was carried out in acetic acid containing a catalytic quantity of pyridine. The nitro derivatives (IIIa, IIIb) so obtained were reduced to the amino derivatives IVa, IVb, and diazotization of the latter in the dark gave the stable dark red crystalline diazonium salts Va, Vb. In acetonitrile solution, these diazonium salts absorbed in the 440-580 nm region (Table 1). These long-wave absorption bands are associated with intramolecular charge transfer from the donor heterocycle fragment of the molecule to the diazonium acceptor.

Exposure of these dithiolylidene-(4′-phenyldiazonium)acetonitrile derivatives (Va and Vb) to visible light led to their decomposition with evolution of nitrogen.

Photolysis quantum yields for compounds Va and Vb in acetonitrile on irradiation at the long wavelength maximum amounted to 0.1 mole/einstein.

EXPERIMENTAL

Electronic and IR spectra were respectively obtained on Specord UV-Vis and Specord IR-75 instruments, the latter as mulls in mineral oil for the 600-2000 cm^{-1} region and in hexachlorobutadiene for 2000-3600 cm^{-1}. Quantum yields of the photodecomposition were determined in acetonitrile solutions. Irradiation was carried out at the maximum of the long wavelength band under conditions of complete absorption. Reinecke salt was used to calibrate the light source [2].

Compounds Ia and Ib were prepared by the method of [3].

Results of the elemental analysis of compounds III-V for C, H, N were in agreement with calculated values.

(4,5-Dimethyl-1,3-dithiolylidene)-(4′-nitrophenyl)acetonitrile (IIIa). 2-Ethylmercapto-4,5-dimethyl-1,3-dithiolium fluoroborate (2.78 g, 0.01 mole) and 4-nitrobenzyl cyanide (1.62 g, 0.01 mole) in 10 ml acetic acid containing 1 ml pyridine were heated at bp for 2.5 h. The mixture was cooled and the precipitate filtered off. The product was recrystallized from ethanol or acetonitrile to give 2.3 g yellow compound IIIa.

(4,5-Ethylenedithio-1,3-dithiolylidene)-(4′-nitrophenyl)acetonitrile (IIIb) was prepared in a similar way to IIIa. Recrystallization from acetonitrile gave the dark red crystalline compound IIIb.

(4,5-Dimethyl-1,3-dithiolylidene)-(4′-aminophenyl)acetonitrile (IVa). To a solution prepared from 5 g stannous chloride, 4 ml acetic acid, and 4 ml concentrated hydrochloric acid was added, gradually with stirring at 60-80°C, 1.45 g (0.005 mole) (4,5-dimethyl-1,3-dithiolylidene)-(4′-nitrophenyl)acetonitrile. Stirring was continued for a further 0.5 h after the compound had dissolved and the solution was then cooled and the amine double salt filtered off and decomposed with 20% aqueous sodium hydroxide. The amine was crystallized from ethanol to give 1.1 g deep yellow crystals of compound IVa.

(4,5-Ethylenedithio-1,3-dithiolylidene)-(4′-aminophenyl)acetonitrile (IVb). Stannous chloride was used to reduce 1.76 g (0.005 mole) (4,5-ethylenedithio-1,3-dithiolylidene)-(4′-nitrophenyl)acetonitrile in the same way as for compound IVa.

Fluoroborate of (4,5-Dimethyl-1,3-dithiolylidene)-(4′-phenyldiazonium)acetonitrile (Va). To a suspension of 0.8 g (0.003 mole) (4,5-dimethyl-1,3-dithiolylidene)-(4′-aminophenyl)acetonitrile in 20 ml concentrated hydrochloric acid was added, gradually with stirring at 5-7°C over 0.5 h, a solution of 0.3 g sodium nitrite in 6 ml water.

The diazonium salt was precipitated by addition of HBF_4 and purified by reprecipitation by ether from nitromethane to give 0.6 g compound Va in the form of a red powder.

Fluoroborate of (4,5-Ethylenedithio-1,3-dithiolylidene)-(4′-phenyldiazonium)acetonitrile (Vb) was prepared and purified in a similar manner to Va.

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